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Free-Flowing Pearlescent Concentrate

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(56) Opposition documents:

European Patent Application 205 922 A

European Patent Application 300 379 A

European Patent Application 376 083 A

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Description

The present invention relates to a pearlescent concentrate in the form of a free-flowing or freely pumpable aqueous dispersion containing components that produce pearlescence in the amount of 15-40 percent by weight.

Aqueous preparations of surfactants and cosmetic preparations may be formulated to have a pearlescent, aesthetically attractive appearance can by incorporating substances which precipitate on cooling to yield fine crystals with a mother of pearl luster that remain dispersed in the preparations. Suitable examples of pearlescing substances include, e.g., the monoesters, diesters and optionally also the triesters of ethylene glycol, propylene glycol and oligomeric alkylene glycols of this type or glycerol with C₁₄-C₂₂ fatty acids, fatty acids and monoalkanol amides of fatty acids.

It is also known that the above-mentioned pearlescing substances can form a stable dispersion in water or in an aqueous surfactant solution, and that concentrated pearlescent dispersions obtained in this way can be added to the preparations that are to be finished to be pearlescent without heating, so that no heating or cooling is necessary to form these pearlescent crystals, although these steps would otherwise be necessary in order to successfully incorporate such substances.

Pearlescent concentrates based on the above-mentioned pearlescing substances are known, for example, from German Patent Application 16 69 152 A, Japanese Patent 56 / 71021 (Chem. Abstr. 95 / 156360), German Patent Application 34 11 328 A, German Patent Application 35 19 081 A and German Patent Application 38 43 572 A.

One problem in the production and use of pearlescent concentrates is their pumpability and free-flowability. Especially at high concentrations of pearlescing components and emulsifiers, the pumpability and free-flowability are often greatly impaired, or the mixtures may not even be free-flowing and thus they cannot be pumped with the conventional equipment.

Therefore, German Patent Application 38 43 572 proposes that the viscosity of pearlescent concentrates be reduced by adding small amounts of low molecular polyhydric alcohols, thereby yielding free-flowing and pumpable preparations.

The present patent application discloses a free-flowing pearlescent concentrate which is characterized in that it contains:

- (A) 15-40 percent by weight pearlescing components
- (B) 5-55 percent by weight nonionic, ampholytic and/or zwitterionic emulsifiers and
- (C) 0.1-5 percent by weight low molecular polyhydric alcohols.

However, the problem of preserving these pearlescent concentrates is addressed only in the usual manner to the extent that the use of known preservatives is recommended to preserve these pearlescent concentrates.

To protect against bacterial and fungal infestations, the known pearlescent concentrates are also treated with preservatives such as organic acids (formic acid, benzoic acid, salicylic acid, sorbic acid), formaldehyde, isothiazolinones, PHB esters or 1,3-dioxanes.

From a dermatological standpoint, however, preservatives can cause various skin diseases and different types of skin irritation. Therefore, more and more body cleansing products and cosmetics that are free of

preservatives have become available recently. In order to impart an esthetically attractive appearance to such products with the use of pearlescent concentrates, as desired by the consumer, there has therefore been a demand for pearlescent concentrates formulated without preservatives. However, this freedom from preservative should not have a negative effect on the microbiological stability of these concentrates or their other properties.

It has now been found that by adding large amounts of low molecular polyhydric alcohols, it is possible to produce pearlescent concentrates that are equivalent to the known pearlescent concentrates with regard to their stability as well as their pumpability and free-flowability.

The present patent application thus relates to a free-flowing pearlescent concentrate in the form of a free-flowing aqueous dispersion, which is characterized in that it contains:

- (A) 15-40 percent by weight pearlescing components,
- (B) 5-55 percent by weight emulsifiers, and
- (C) 15-40 percent by weight low molecular polyhydric alcohols with two to six carbon atoms and two to six hydroxyl groups.

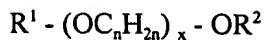
Especially advantageous properties are shown by pearlescent concentrates that contain:

- (A) 20-30 percent by weight pearlescing components,
- (B) 10-35 percent by weight emulsifiers, and
- (C) 20-40 percent by weight alcohols with two to six carbon atoms and two to six hydroxyl groups.

The term 'pearlescing components' is understood to refer to meltable fatty or waxy substances that crystallize out in the form of fine pearlescent crystals on cooling of their aqueous solutions or emulsions in a temperature range of approximately 30-90°C.

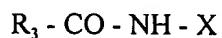
Such meltable fatty or waxy substances include

- (A1) esters of formula (I),



where R^1 is a linear fatty acyl group with 14 to 22 carbon atoms, R^2 is hydrogen or an R^1 group, $n = 2$ or 3 and x is a number from 1 to 4,

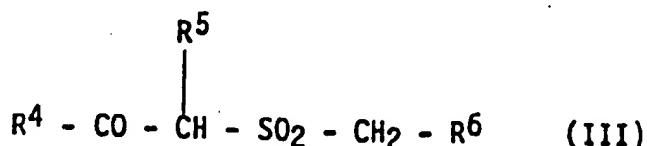
- (A2) monoalkanolamides of general formula (II)



where R^3 is an alkyl group with 8 to 22 carbon atoms, in particular with 8 to 18 carbon atoms, and X is a $-CH_2-CH_2-OH$ group, a $-CH_2-CH_2-CH_2-OH$ group or a $-C(CH_3)_2-OH$ group,

- (A3) linear, saturated fatty acids with 14 to 22 carbon atoms and

- (A4) β -keto sulfones of general formula (III),



where R⁴ is an alkyl group or an alkenyl group with 11 to 21 carbon atoms, R⁵ and R⁶ or together they may form an ethylene group which, together with the group between R⁵ and R⁶, forms a tetrahydrothiophene dioxide ring.

(A5) mono-, di- and triesters of glycerol with linear saturated fatty acids with 14 to 22 carbon atoms.

Suitable esters (A1) of general formula R¹(OC_nH_{2n})_xOR² include the mono- and diesters of ethylene glycol and propylene glycol with higher fatty acids, e.g., palmitic acid, stearic acid or behenic acid or the diesters of diethylene glycol or triethylene glycol with such fatty acids. Mixtures of mono- and diesters of these glycols with fatty acid mixtures such as hardened tallow fatty acid or with the saturated C₁₄-C₁₈ fatty acid fraction of tallow fatty acid are also suitable. The ethylene glycol mono- and/or diesters of palmitic acid and/or stearic acid are preferred.

Preferred monoalkanol amides (A2) include the monoethanol amides. These compounds may contain a uniform alkyl group. However, the production of alkanol amides may conventionally also begin with fatty acid mixtures of natural sources, such as coconut fatty acids in preparing the alkanol amides, so that the resulting products are the corresponding mixtures with regard to the alkyl groups.

Examples of suitable linear fatty acids (A3) include, e.g., palmitic acid, stearic acid, arachidic acid or behenic acid, but it is also suitable to use a technical grade fatty acid cut which consists mostly or entirely of fatty acids with 16 to 22 carbon atoms such as the palmitic acid-stearic acid fractions obtained from tallow fatty acid by separating the fatty acids that are liquid at +5°C or palmitic acid-stearic acid fractions such as those accessible by hardening tallow fatty acid.

In comparison with the known ethylene glycol mono- and diesters, the β-keto sulfones (A4) of general formula (III) have the advantage that the pearlescence of the preparations has greater thermal stability, i.e., they retain their pearlescence for several hours, even when the preparations are heated to temperatures above 50°C, in some cases even to more than 70°C. For additional information about the above-mentioned β-keto sulfones, the reader is referred explicitly to the contents of German Patent Application 35 08 051.

The esters of glycerol (A5) that can be used in the teaching according to this invention include the mono-, di- and especially the triesters of myristic acid, palmitic acid, stearic acid and behenic acid as well as mixtures of these fatty acids.

Fatty alcohols with at least 20 carbon atoms, in particular those with 20 to 30 carbon atoms may also be used as the pearlescent concentrates.

The pearlescent concentrates according to this invention may contain representatives of only one of these classes of compounds or they may also contain mixtures of representatives of several of these classes of compounds.

Representatives of classes (A1) through (A3) are preferred pearlescent concentrates.

However, fatty acid mono- and dialkanolamides, i.e., the pearlescent components of group (A2) and their derivatives, have recently been suspected of involvement in the formation of nitrosamines. Therefore, it may be desirable to formulate cosmetic preparations without using such alkanolamines and alkanolamine derives. For this reason, the compounds of classes (A1) and (A3) may be especially preferred pearlescing components.

Pearlescent concentrates in which the pearlescing components consist of at least 70 percent by weight, in particular at least 90 percent by weight, ethylene glycol distearate are especially preferred.

Emulsifiers (B) that can be used include ionic or nonionic surfactant compounds which are characterized by a lipophilic group, preferably a linear alkyl or alkenyl group, and at least one hydrophilic group. This hydrophilic group may be an ionic or a nonionic group.

Suitable anionic emulsifiers (B) include, for example, alkyl sulfates and alkyl polyethylene glycol ether sulfates with 8 to 22 carbon atoms in the alkyl chain and 1 to 15, in particular 1 to 6 ethylene glycol ether groups in the molecule, which are used in the form of their alkali salts, magnesium or ammonium salts, mono-, di- or trialkanol ammonium salts with 2 to 3 carbon atoms in the alkanol group. Other suitable anionic surfactants include alkane sulfonates, α -olefin sulfonates, α -sulfo fatty acid methyl esters, fatty alcohol (polyglycol ether) carboxylates, sulfosuccinic acid, mono- and dialkyl esters, sulfosuccinic acid ester salts, acyl isethionates, acyl taurides and acyl sarcosides, each with 8 to 22 carbon atoms, in particular 12 to 18 carbon atoms in the alkyl or acyl chain. Soaps may also be used as emulsifiers. This may be achieved, for example, by converting a small portion, i.e., approximately 1 to 20 percent by weight, of the linear saturated fatty acids to an anionic emulsifier by the addition of alkali hydroxide.

Preferred anionic emulsifiers include alkyl polyethylene glycol ether sulfates, e.g., sodium lauryl polyglycol ether sulfate.

Suitable cationic emulsifiers (B) include quaternary ammonium surfactants, e.g., alkyl trimethyl ammonium chlorides and dialkyl dimethyl ammonium chlorides, e.g., cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride and lauryl dimethyl benzyl ammonium chloride, cetyl pyridinium chloride and tallow alkyl tris-(oligoxyalkyl) ammonium phosphate.

Furthermore, emulsifiers (B) may also include zwitterionic surfactants. The term "zwitterionic surfactants" refers to surface-active compounds having at least one quaternary ammonium group and at least one $-\text{COO}^-$ group or $-\text{SO}_3^-$ group in the molecule. Especially suitable zwitterionic surfactants include betaines such as N-alkyl-N,N-dimethyl ammonium glycinate, e.g., coconut alkyl dimethyl ammonium glycinate, N-acyl-aminopropyl-N,N-dimethyl ammonium glycinate, e.g., coconut acylaminopropyl-dimethyl ammonium glycinate and 2-alkyl-3-carboxymethyl-3-hydroxyethyl-imidazolines, each with 8 to 18 carbon atoms in the alkyl or acyl group as well as coconut acylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known by the CTFA terminology cocamidopropyl betaine is especially preferred.

Other suitable emulsifiers (B) include ampholytic surfactants. Ampholytic surfactants are understood to refer to surface-active compounds having at least one free amino group and at least one $-\text{COOH}$ - or $-\text{SO}_3\text{H}$ - group in the molecule in addition to a $\text{C}_8\text{-C}_{18}$ alkyl or acyl group; these compounds are capable of forming internal salts. Examples of suitable ampholytic surfactants include N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkyl-iminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids, each with approximately 8 to 18 carbon atoms in the alkyl group. Especially

preferred amphotytic surfactants include N-coco alkyl aminopropionate, coco acyl aminoethyl aminopropionate and C₁₂-C₁₈ acylsarcosine.

Finally, it is also possible to use nonionic emulsifiers (B) which contain as the hydrophilic group, e.g., a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups. Such compounds include, for example:

- (B1) addition products of 2 to 30 mol ethylene oxide and/or 0 to 5 mol propylene oxide onto linear fatty alcohols with 8 to 22 carbon atoms, onto fatty acids with 12 to 22 carbon atoms and onto alkyl phenols with 8 to 15 carbon atoms in the alkyl group,
- (B2) C₁₂-C₂₂ fatty acid monoesters and diesters of addition products of 1 to 30 mol ethylene oxide onto glycerol,
- (B3) glycerol monoesters and diesters and sorbitan monoesters and diesters of saturated and unsaturated C₈-C₂₂ fatty acids and their ethylene oxide addition products,
- (B4) C₈-C₂₂ alkyl monoglycosides and oligoglycosides as well as their ethoxylated analogs and
- (B5) addition products of 5 to 60 mol ethylene oxide onto castor oil and hardened castor oil.

Mixtures of compounds from several of these classes of substances are also suitable.

Addition products of ethylene oxide and/or propylene oxide onto fatty alcohols, fatty acids, alkyl phenols, glycerol monoesters and diesters and sorbitan monoesters and diesters of fatty acids or onto castor oil are known products that are commercially available. They are homolog mixtures with an average degree of alkoxylation corresponding to the ratio of the substance quantities of ethylene oxide and/or propylene oxide and the substrate with which the addition reaction is carried out.

C₁₂-C₂₂ fatty acid monoesters and diesters of the addition products of ethylene oxide onto glycerol are known from German Patent 20 24 051 as moisturizing agents for cosmetic preparations. C₈-C₂₂ alkyl mono- and oligoglycosides, their synthesis and use as surfactants are disclosed, for example, in U.S. Patent Application 3,839,318 A, U.S. Patent Application 3,707,535 A, U.S. Patent Application 3,547,828 A, German Patent Application 19 43 689 A, German Patent Application 20 36 472 A and German Patent Application 30 01 064 A as well as European Patent Application 77 167 A. In particular, they are synthesized by reacting glucose or oligosaccharides with primary alcohols having 8 to 22 carbon atoms. With regard to the glycoside group, it is true that both monoglycosides in which a cyclic sugar group is bound by a glycoside bond to the fatty alcohol as well as oligomeric glycosides with a degree of oligomerization of up to preferably approximately 8 are suitable. A degree of oligomerization of 1.4 or less may be especially preferred. The degree of oligomerization is a statistical average based on a homolog distribution which is conventional for such technical grade products.

Compounds from group (B1) are especially preferred nonionic emulsifiers (B) as part of the teaching according to the present invention.

The compounds with alkyl groups used as surfactants here may be uniform substances, but it is usually preferable to start with native animal and vegetable raw materials in synthesizing these substances, so that substance mixtures with different alkyl chain lengths are obtained, depending on the raw material used in each case.

The surfactants which are the addition products of ethylene oxide and/or propylene oxide onto fatty alcohols may include products with a "normal" homolog distribution as well as those with a narrow homolog distribution. A "normal" homolog distribution is understood to refer to mixtures of homologs which are obtained by reacting fatty alcohol and alkylene oxide using alkali metals, alkali metal

hydroxides or alkali metal alcoholates as catalysts. However, a narrow homolog distribution is obtained when using hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides or hydroxides or alcoholates as catalysts. Using products with a narrow homolog distribution may be preferred.

The pearlescent concentrates according to this invention may contain representatives of one or more of the above-mentioned classes of surfactants.

Anionic emulsifiers are preferred as emulsifiers (B) because pearlescent concentrates are added mainly to formulations containing anionic surfactants.

In addition, the pearlescent concentrates according to this invention which contain only nonionic, zwitterionic and/or ampholytic surfactants have proven to be universally suitable and to be especially compatible with aqueous preparations of water-soluble surfactants of any desired type and ionicity. Therefore, the use of these classes of surfactants is also especially preferred.

The deciding factor in the pumpability and free-flowability of the pearlescent concentrates according to this invention and their resistance to bacteria and fungi is that they contain alcohols with two to six carbon atoms and two to six hydroxyl groups. Such alcohols include, for example, ethylene glycol, 1,2- and 1,3-propylene glycol, glycerol, di- and triethylene glycol, erythritol, arabitol, adonitol, xylitol, sorbitol, mannitol and dulcitol. The use of glycerol, 1,2-propylene glycol, 1,3-propylene glycol and/or sorbitol is especially preferred.

Using glycerol as the alcohol leads to pearlescent concentrates that impart an especially brilliant pearlescence to the end products.

In addition to these ingredients, the pearlescent concentrates according to this invention contain mainly water.

In addition, buffer substances may also be added in subordinate amounts to adjust the pH to values between 2 and 8; such buffer substances include citric acid and/or sodium citrate as well as inorganic salts such as sodium chloride as thickeners.

Although the pearlescent concentrates according to this invention are usually free of preservative, subordinate amounts of conventional commercial preservatives may also present in exceptional cases and may be introduced through individual raw materials, for example.

The pearlescent concentrates according to this invention remain pumpable in a temperature range of at least 5°C to 40°C and they are stable in storage for a long period of time, e.g., at least about three months.

The pearlescent concentrates according to this invention are preferably prepared by first heating components (A), (B) and (C) together to a temperature about 1 to 30°C above the melting point. In most cases, this temperature will be about 60 to 90°C. Then, water which has been heated to approximately the same temperature is added to this mixture. If the emulsifier used is an ionic, water-soluble surfactant, it may preferably be dissolved in the aqueous phase and added to the mixture together with the water. The aqueous phase may optionally also contain the dissolved buffer substances. The resulting dispersion is then cooled to room temperature, i.e., about 25°C, while stirring constantly. The viscosity of the pearlescent concentrate is usually so low that no special stirring equipment such as homogenizers or other high-speed mixing equipment need be used.

The pearlescent concentrates according to this invention are suitable for producing liquid, aqueous, opaque and pearlescent preparations of water-soluble surfactants. They may be incorporated into liquid detergents and cleaning agents such as dishwashing products, liquid fine fabric detergents and liquid soaps, preferably liquid body cleansing and care products such as shampoos, hand and body washing liquids, shower gels and other preparations, bath additives (bubble baths), hair rinses or hair dyeing preparations.

To produce a pearlescence, pearlescent concentrates according to this invention are added to the clear aqueous preparations in an amount of 0.5 to 10 percent by weight, especially 1.5 to 5 percent by weight, at 0 to 40°C and distributed therein by stirring. This yields a metallic shiny, highly to weakly shiny, extremely dense pearlescence, depending on the preparation and the concentration in which it is used.

The following examples are presented to illustrate the object of the present invention in greater detail without limiting the scope in any way.

Examples

1. Pearlescent concentrates

Pearlescent concentrates having the compositions listed in Table 1 were prepared. The substances listed with their commercial brand names are the substances listed below:

1. Ethylene glycol distearate (at least 90% diester) (Henkel)
2. Coco fatty acid monoethanol amide (CTFA designation: cocamide MEA (approx. 95% amide)) (Henkel)

Composition of the fatty acid:	approx. 56% lauric acid approx. 21% myristic acid approx. 10% palmitic acid approx. 13% stearic acid and oleic acid
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3. Mixture of palmitic acid and stearic acid (approx. 1:1)
4. Fatty alcohol polyglycol ether sulfate (CTFA designation: laureth-10 (approx. 74% C₁₂-C₁₄ fatty alcohol)) (Henkel)
5. Sodium lauryl ether sulfate (CTFA designation: sodium laureth sulfate (approx. 72% active substance)) (Henkel)
6. C₁₂-C₁₄ fatty alcohol + 3 ethylene oxide units (Henkel)
7. Aqueous solution of a fatty acid amide derivative with a betaine structure of the formula R-CONH-(CH₂)₃-N⁺(CH₃)₂-CH₂-COO⁻ (CTFA designation: cocamidopropyl betaine (approx. 30% active substance, approx. 5% NaCl)) (Henkel)
8. C₁₂-C₁₄ fatty alcohol + 3 ethylene oxide units (Henkel)
9. Polyol fatty acid ester (CTFA designation: PEG-7-glyceryl cocoate) (Henkel)

Table 1: Free-flowing pearlescent concentrate Content (percent by weight, wt%)

Practical examples

1) Shower soap

	Parts by weight
Texapon® N 25 ¹¹	35
Dehyton® K	7
Lamepon® S ¹²	5
Pearlescent concentrate 1	3
Water	to a total of 100

Then the viscosity of the shower soap was adjusted to a level of 4000 mPas by adding sodium chloride.

- 11. ¹ Sodium lauryl ether sulfate (CTFA designation: sodium laureth sulfate (approx. 28% active substance in water)) (Henkel)
- 12. Protein hydrolysate fatty acid condensate potassium salt (CTFA designation: potassium coco hydrolyzed animal collagen) (Henkel)

2) Mild shampoo

	Parts by weight
Texapon® ASV ¹³	14
Texapon® SB3 ¹⁴	10
Dehyton® G ¹⁵	14
Nutrilan® I 50 ¹⁶	2.5
Pearlescent concentrate 2	2
Water	to a total of 100

Then the viscosity was adjusted to a level of 5000 mPas by adding sodium chloride and Arlypon® F (ethoxylated fatty alcohol with a narrow homolog distribution) (Henkel)).

- 13. Mixture of special fatty alcohol ether sulfates (CTFA designation: sodium laureth sulfate (and) magnesium laureth sulfate (and) sodium laureth 8-sulfate (and) magnesium laureth 8-sulfate (and) sodium oleth sulfate (and) magnesium oleth sulfate (approx. 30% active substance in water)) (Henkel)

¹ Translator's note: There was no "10" in this series.

14. Sulfosuccinic acid semiester based on an alkyl polyglycol ether, disodium salt (CTFA designation: disodium laureth sulfosuccinate (approx 40% active substance in water)) (Henkel)
15. Fatty acid amide derivative with an amphoteric character (N-hydroxyethyl-N-coco alkylamidoethyl glycinate sodium salt) (CTFA designation: coco amphodiacetate (approx. 30% active substance in water)) (Henkel)
16. Partial protein hydrolysate from degraded bovine collagen (CTFA designation: hydrolyzed animal protein) (Henkel)

3) Bubble bath

Parts by weight	
Texapon® N 40 ¹⁷	40
Dehyton® K	6.5
Dehyton® G	6.5
Cetiol® HE	5
Pearlescent concentrate 3	5
Water	to a total of 100

Then the viscosity was adjusted to 6000 mPas by adding sodium chloride.

17. Sodium lauryl ether sulfate (CTFA designation: sodium laureth sulfate (approx. 285 active substance in water)) (Henkel)

[Claims are in English]